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Development of a petrographic classification of fly-ash components from coal combustion and co-combustion. (An ICCP Classification System, Fly-Ash Working Group – Commission III.)

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ABSTRACT

A new system for the microscopic classification of fly-ash components has been developed by the Fly-Ash Working Group, Commission III of the ICCP and is presented herein. The studied fly-ashes were obtained from the combustion of single coals of varied rank, coal blends, and coals blended with other fuels (biomass, petroleum coke), in different operating conditions and by means of different technologies. Microscopic images of the fly-ash samples were used to test the optical criteria proposed for classifying the fly-ash components.

The classification system developed is based on a small number of microscopic criteria, subdivided into six independent levels or categories, three of which are directed at whole particle identification on the basis of nature, origin and type of fly-ash particle, while the other three levels are directed at the smaller section identification on the basis of character, structure and optical texture of unburned carbons. To classify the inorganic components of the fly-ash, the criterion proposed is composition in terms of metallic/non-metallic character. To establish the classification criteria the petrographers involved in the work performed three successive round robins.

Evaluation of the results by using firstly descriptive statistics and then the criteria and parameters employed by the ICCP in their accreditation programs indicated that the classification of the fly-ash components was accurate and that there was only a minor bias. The main conclusion of this study was that the proposed criteria are valuable for identifying, and classifying fly-ash components and for describing the optical properties of fly-ash particles.

1. Introduction

Fly-ash is one of the residues generated during coal combustion and co-combustion (coal and other feed materials such as biomass, tires, wastes, etc.). Fly-ashes are fine particles that rise with the flue gases and are captured by electrostatic precipitators, bag-houses or cyclones before the flue gases are released to the atmosphere. Fly-ashes are

composed of an inorganic fraction which is always the predominant one and an organic fraction, the so-called unburned carbons or fly-ash carbons, which may include: soot (carbon nanospheres); solid carbonaceous residue or char; and volatile organic compounds that may condense on the char surface to form pyrocarbon rims.

Fly-ash may be stored at the coal power plants, or they may be deposited in landfills and dumps resulting in extra management costs

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and negative environmental impact. For this reason, the best solution for the fly-ash is to be reused. Fly-ash can find applications in many fields such as the cement (Portland cement) and concrete industry, brick making industry, asphalt and concrete plants, waste treatment and soil stabilization, and geopolymers, among others. In all cases the different uses of fly-ashes depend on their composition, which is regulated by the ASTM C618 (2015) norm according to which fly-ash is grouped into classes C and F:

- Class C fly-ash is produced from combustion of lignite and sub-bituminous coal and has pozzolanic and some self-cementing properties. It generally contains > 20% CaO, and alkali and sulfate contents are high in this C class of fly-ash.
- Class F fly-ash derives from combustion of medium and high rank coals (see ISO 11760, 2005 for coal classification). This fly-ash is pozzolanic in nature, and contains < 20% CaO.

Because industrial classification of fly ash relies on inorganic matter, the inorganic fraction has received much more attention than the organic fraction (unburned carbons).

1.1. Unburned carbon from fly-ashes

The unburned carbons from fly-ashes are also important because of their peculiar physico-chemical properties, which may also have an impact e.g., on the air-entraining mixtures in concrete production and the alteration of concrete with time. In general, these unburned carbons have been characterized and investigated as a whole and although a few attempts have been made to classify the various forms of carbon, no comprehensive, useful or practical classification of fly-ash carbons has yet been developed. A comprehensive classification is necessary since the different fly-ash carbons have their own distinctive physico-optical and textural properties (Hower et al., 1995, 1996, 1999, 2000a,b, 2005a; Hower and Mastalerz, 2001; Suárez-Ruiz et al., 2006, 2007) and not all fly ash-carbons behave in the same way, for example in their capacity to retain trace elements (Hower et al., 1996, 1999, 2000b; Suárez-Ruiz et al., 2006, 2007) or when they are used as precursors for carbon materials (e.g., Hower et al., 2000a; Suárez-Ruiz et al., 2007; Girón et al., 2015). Other works report on the relationships between the surface area and the porosity of coal fly-ash and their carbon content (Schure et al., 1985). The nature of fly-ash carbons, their porosity, polarity, and optical properties, the influence of these properties on the adsorption of air-entraining admixtures (AEAs), and the size distribution of the carbons in relation to their surface area and accessibility in AEAs adsorption for both classes (C and F) of fly-ashes have been investigated by Baltrus et al. (2001); Gao et al. (1997); Külaots et al. (2004); Lee et al. (1999); Lyster and Stanmore (1995); Sarbak et al. (2004) among others. Fly-ash carbons have also been considered as being suitable for the development of sorbents (Akgerman and Zardkoohi, 1996; Li et al., 2006; Lee et al., 2006; Snape et al., 2004). The preparation of activated carbons, and in general the use of unburned carbons as precursors for other materials has been investigated by many authors (Baltrus, et al., 2001; Li et al., 2006). The main conclusion from all these research works is that the various fly-ash carbons have different properties which depend on their origin or feed fuel (Baltrus, et al., 2001; Külaots et al., 2004), and operating conditions during the process of combustion.

Interest in the development of a classification of fly-ash components dates back to the twenties of the last century when Newall and Sinnatt (1924), Sinnatt et al. (1927), and Sinnatt and Slater (1922) called the carbonaceous hollow spherical shells “cenospheres”. However, only in the 1950s in the USA., was the importance of unburned carbons recognised again due to the growing interest in atmospheric pollution (Drinker and Hatch, 1954; Hamilton and Jarvis, 1963; McCrone and Delly, 1973), but the first fly-ash nomenclature schemes were not presented until the late 1970s (Fisher et al., 1978), and early 1980s

(Ramsden and Shibaoka, 1982).

1.2. Chars and fly-ash microscopy

Over time a great amount of research and numerous petrographical studies on fly-ash and chars have been reported such as those by: Alonso et al. (2001); Álvarez et al. (1997); Alpern and Chauvin (1958); Alpern (1961, 1965); Alpern et al. (1957, 1960); Bailey et al. (1990); Bend (1989); Bend et al. (1992); Bengtsson (1986, 1987); Bourrat et al. (1986); Bruckhorst (1994); Cloke and Lester (1994); Crelling et al. (1992); Diessel and Wolff-Fischer (1987a,b); Goodarzi and Vleeskens (1988); Griest and Harris (1985); Gupta (2007); Hower et al. (1995, 1996, 1999, 2000a,b, 2005a); Hower and Mastalerz (2001); Jones et al. (1985a,b); Kleesattel et al. (1987); Lee and Whaley (1983); Lester et al. (1993, 1996, 2000, 2010); Lightman and Street (1968); Littlejohn (1967); McCrone and Delly (1973); Menéndez et al. (1993); Nandi et al. (1977); Oka et al. (1987); Petersen (1998); Phong-Anant et al. (1989); Ramsden and Shibaoka (1982); Rosenberg et al. (1996a,b); Shibaoka (1969a,b, 1985); Shibaoka et al. (1985, 1989); Skorupska et al. (1987); Street et al. (1969); Suárez-Ruiz et al. (2006, 2007); Suárez-Ruiz and Valentim (2007); Tang et al. (2005); Thomas et al. (1993a,b); Tsai and Scaroni (1984, 1987a,b); Valentim et al. (2006, 2009, 2011, 2013); Vleeskens and Malechaux (1986); Vleeskens and Nandi (1986); Vleeskens et al. (1988, 1993); Young et al. (1987); Yu et al. (2007), among others.

Two of the most complete classifications of chars (as a proxy of fly-ash components) by optical microscopy deserve to be highlighted. The first one was developed by Bailey et al. (1990) who established a char classification system that can be applied to coal combustion residues from subbituminous and bituminous coals. This classification was based on morphological, porosity and char wall thickness criteria. However, when this classification is applied to fly-ash it fails to cover all the residues found in fly-ashes, e.g., it does not cover residues from the combustion of high-rank coals. The second classification is the very detailed ICCP Char Classification (Lester et al., 2000, 2010), which does not take into account the fact that the inorganic phases are the main components of fly-ash, and spinels, quartz and glassy material are all combined under the heading “mineroid” (Fig. 1A, B). Again, this classification does not cover all types of organic particles found in fly-ash, and does not fit well with some types of fly-ash carbons, e.g., “inertoid” is a designation that includes either one char particle developed during pyrolysis, with a very low porosity (lower than 40%), unfused, isotropic, and probably derived from inertinite, and an anisotropic unburned carbon derived from the combustion of an anthracitic vitrinite (Fig. 1C, D).

Other pre-existing classifications specifically focused on fly-ash components (e.g., Hower and Mastalerz, 2001; Hower et al., 2005a) are based on genetic and textural criteria, but either they are very difficult to handle due to the detailed descriptions and the use of numerical codes, or they are incomplete and do not cover all types of particles that can be found in fly-ash. For example in Hower and Mastalerz (2001: *vide p. 1320*) and Hower et al. (2005a: *vide p. 653*) the following classification is used:

- (i) the first two categories (“Isotropic” and “Anisotropic carbons”) are derived from the combustion of vitrinite and inertinite. However, “Inertinite” belongs to the third category, and particles derived from combustion of inertinite can also be isotropic or anisotropic carbons;
- (ii) if inertinite is present, then it should be included in the “Uncombusted coal” category;
- (iii) the “Petroleum coke” category should be included in “Other organics” like natural coke.

All of these classifications have the merit of providing a practical solution for fly-ash classification (e.g., Hower and Mastalerz, 2001;

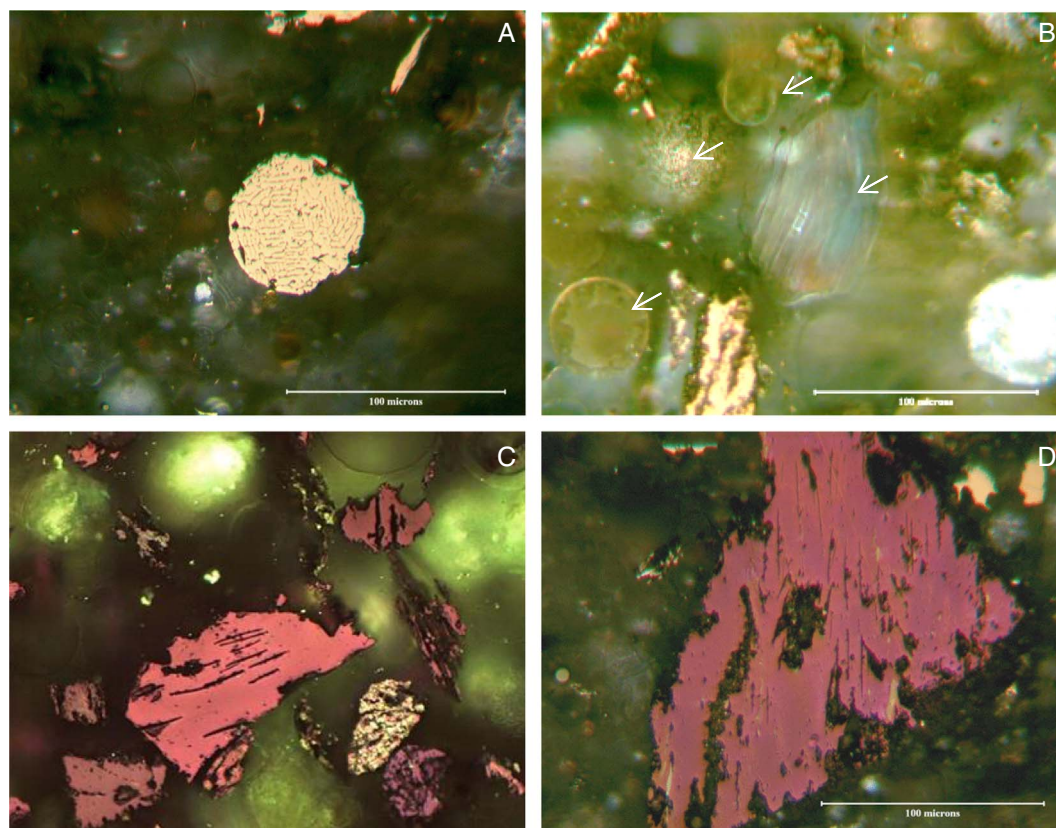


Fig. 1. Optical microscopy photomicrographs. These and all photomicrographs were taken with oil immersion objective of $50\times$, polarized light, and 1λ retarder plate. Examples of mineral matter and inertoids: A) spinel; B) non-metallic mineral matter (arrows); C) inertoid; D) inertoid derived from anthracitic vitrinite. (Long side of the image is $\sim 200\mu\text{m}$).

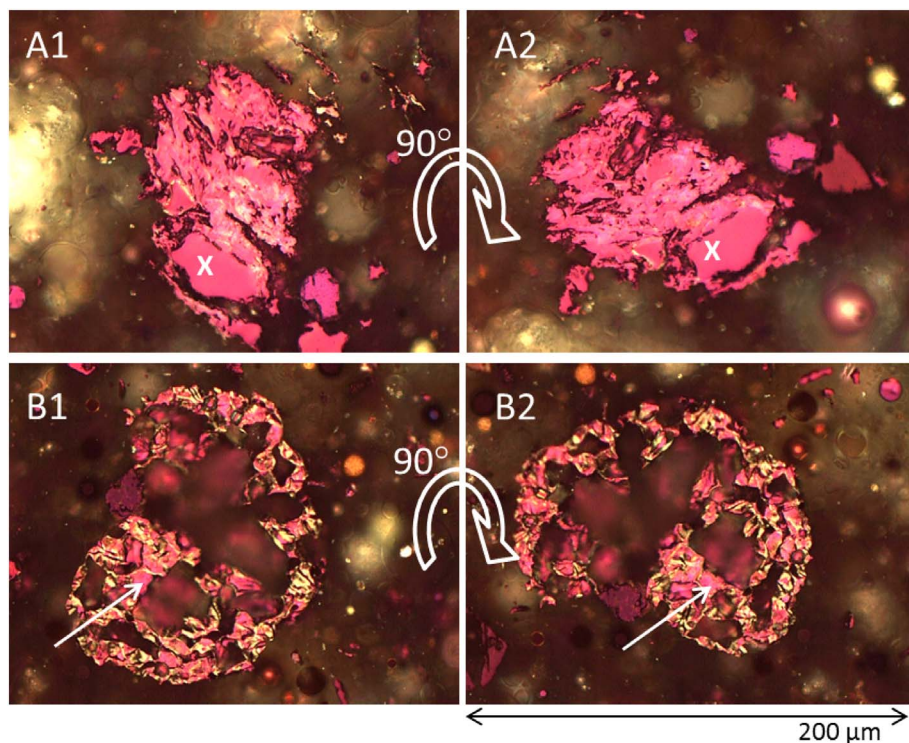


Fig. 2. Example of images of the first fly-ash classification round robin exercise using the cross and arrow pointing system.

Hower et al., 2005a) by facilitating the development of a nomenclature and setting clear limits for the morphotype parameters (Lester et al., 2010). However, these classifications are directed at classifying the whole particle rather than for classifying the specific characteristics,

textures and structures that fly-ash carbons show, thereby contributing only to a partial description of the characteristics of the unburned carbons. Consequently, the problem that needs to be addressed when classifying the fly-ash components is the following: Should the

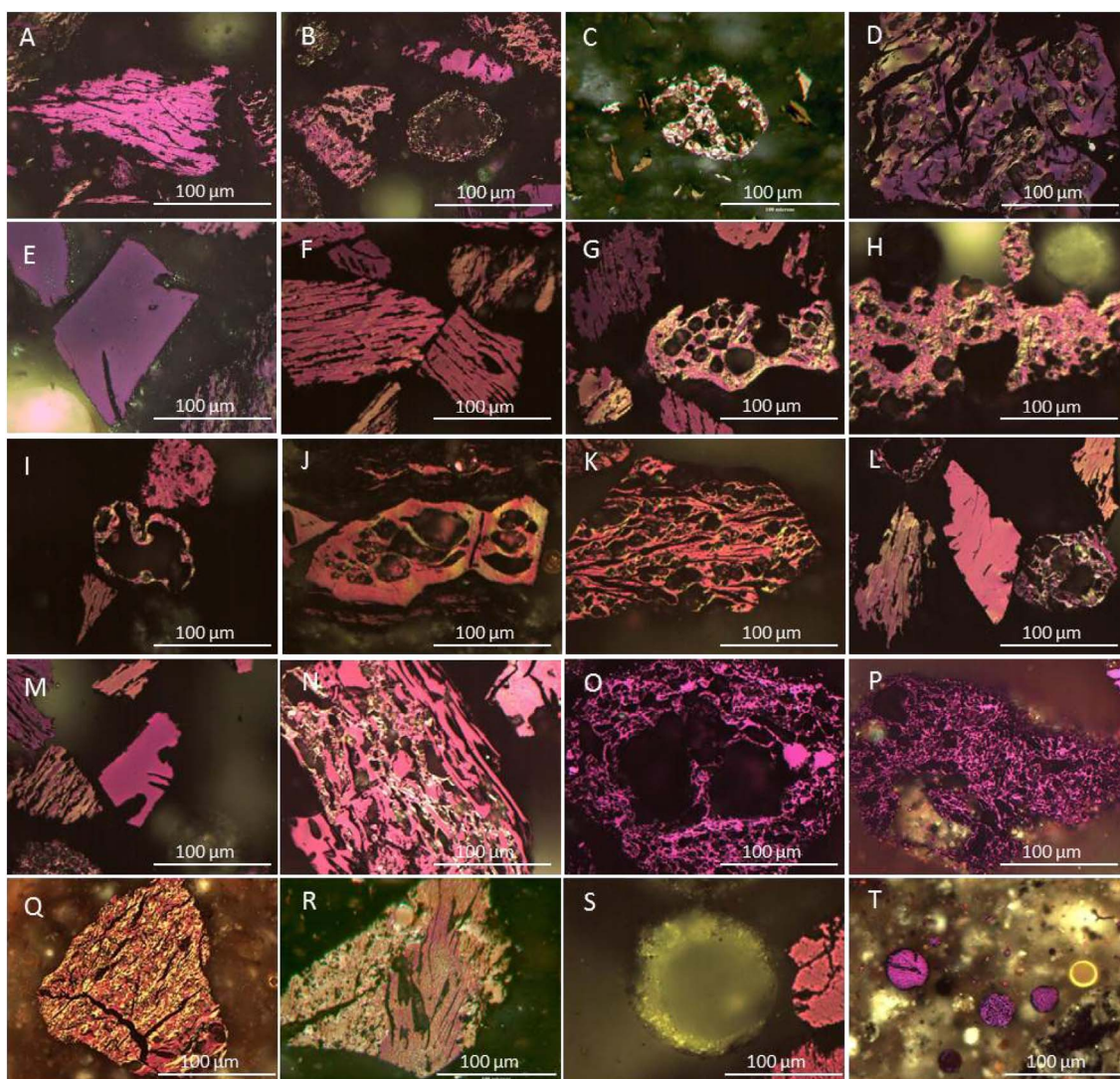


Fig. 3. Examples of unburned carbons in fly-ash: A) anisotropic unfused from vitrinite; B) anisotropic fused from vitrinite; C) anisotropic from pet coke; D) anisotropic from inertinite; E) isotropic unfused from inertinite; F) massive, anisotropic, unfused from high rank (anthracite) vitrinite; G) porous, anisotropic, fused from high rank (semi-anthracite) vitrinite; H) porous, anisotropic, fused from high rank (semi-anthracite) vitrinite; I) porous, anisotropic, fused from medium rank vitrinite; J) porous, vesiculated, anisotropic, fused from inertinite; K) porous, vesiculated, anisotropic, partially fused from Inertinite; L) massive, isotropic from high rank (anthracite) vitrinite; M) massive, isotropic, unfused from inertinite; N) isotropic, unfused from inertinite retaining the original structure; O) porous, isotropic, fused from low-rank vitrinite; P) porous, isotropic, fused from low-rank coal; Q) Petroleum coke, anisotropic; R) Natural coke, anisotropic; S) glassy material; T) spinels (purple spheres) and glassy material (yellow sphere). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

classification be directed towards the whole particle or, as in the case of analysis by means of a point counter on petrographic particulate pellets, should the classification be directed at the field or section at which the cross-hair is pointing? This is an important question because there are particles that contain sections that are, e.g., porous and sections that are massive, fused sections and unfused ones, and the same problem affects anisotropy (see examples in Figs. 2 and 3).

On the other hand a classification needs to be easy to handle and, therefore, should be based on a few selected criteria related to the physico-optical properties of the fly-ash components. However, such a classification should include not only all the morphotypes of unburned carbons that may be found in fly-ashes as a result of the combustion of coal and blends, but also the unburned carbons derived from the co-combustion of coals and other materials.

Taking into consideration the points discussed above, a working group on “The identification and petrographic classification of components in fly-ashes” was created at the Annual Meeting of ICCP, Commission III, in 2005 in Patras (Greece), with the aim of identifying all the organic and inorganic components in fly-ashes by means of

optical microscopy, and to establish an internationally accepted ICCP classification easy to handle and apply (ICCP, 2005).

During the 58th ICCP meeting, held in Bandung (Indonesia) in 2006, the ICCP Commission III members decided that the tasks of classification should begin with a round robin exercise to classify the fly-ash components following three main criteria (ICCP 2006) that should be applied in conjunction with each other (Suárez-Ruiz et al. 2006, 2007) as follows:

- (i) Differentiate the organic and inorganic components;
- (ii) In the case of the organic components, take into account their optical texture, fused or un-fused character, structure and morphology, and origin (coal, others), in that order;
- (iii) In the case of inorganic components, classify them into two categories: metallic and non-metallic components.

The definitions of concepts such as “fused and unfused” character, and “porous and massive/dense” structure are based on the criteria established by the “Inertinite in Combustion WG” of the ICCP (<http://>

Table 1

Glossary of pre-classification categories of microscopic components identified in fly-ash.

Organic fraction

The organic fraction includes fly-ash carbons (anisotropic and isotropic unburned carbons) exclusively derived from coal combustion (combustion of coal macerals), and particles classified as "other organics" which are carbons from petroleum coke, natural coke, and unburned coal fragments. This last category can be composed of either anisotropic or isotropic carbons.

A) Unburned carbons exclusively derived from coal (macerals) combustion**1. Anisotropic**

1.1. Porous and vesiculated particles from the combustion of vitrinite of semi-anthracite and bituminous coal rank: Fused particles, porous and strongly vesiculated particles, developing a spherical hollow structure (the carbon cenosphere) or a network-like structure with few chambers. These carbons develop diverse coke anisotropic domains depending on the coal rank. SEM images of these fly ash carbons usually show perforated spheres.

1.2. Massive particles derived from the combustion of vitrinite of anthracitic/meta-anthracitic coal rank: Unfused particles, with an homogeneous and uniform anisotropy, may show some cracks and very small porosity in the majority of the cases although the porosity cannot always be detected by optical microscopy. SEM images of these fly-ash carbons show unfused particles of variable and irregularly distributed porosity. These carbons show an angular and irregular morphology.

1.3. Porous and vesiculated particles from the combustion of inertinites: Fused or partially fused particles, irregularly porous and vesiculated, with cracks, developing a network-like structure. These carbons are anisotropic to strongly anisotropic. However, they show a sweeping anisotropy totally different to that shown by the other anisotropic fly ash carbons.

1.4. Massive particles from inertinite combustion: Relatively massive particles, partially fused with a low porosity.

1.5. Undifferentiated anisotropic fragments: Small anisotropic carbons, $\leq 10\text{--}15\text{ }\mu\text{m}$, which cannot be assigned to any of the previously described categories of carbons.

2. Isotropic

2.1. Porous and vesiculated particles from the combustion of vitrinite of low rank coals: Fused particles, vesiculated and porous developing structures like cenospheres and networks.

2.2. Massive particles derived from the combustion of inertinite: Totally isotropic particles, unfused or partially fused with variable porosity.

2.3. Particles from inertinite retaining their original structure: Unfused particles with partially to well-preserved original structure.

2.4. Undifferentiated isotropic fragments: Small isotropic particles smaller than $10\text{--}15\text{ }\mu\text{m}$, massive, irregular or vesiculated, that cannot be assigned to any of the previously described categories.

3. Unburned and/or oxidized coal particles: Mainly isotropic particles if derived from bituminous coal rank. Various macerals can be identified: vitrinite, liptinite or inertinite.**B) Other organics (i.e., carbons which are not derived from coal combustion).**

1. Particles from pet coke.

2. Particles from natural coke: found in fly ashes derived from combustion of very high rank coals.

3. Particles from tires: anisotropic particles, irregular, massive or vesiculated.

Inorganic fraction

Categories defined in Hower and Mastalerz (2001) and Hower et al. (2005) including glassy material (that is aluminosilicates with smaller amounts of Fe, Ca, and other elements), quartz, oxides, mullite, spinels, sulfides, sulphates, and "other mineral matter" (inorganic matter that, because of its size and / or the microscope resolution cannot be clearly identified and assigned to any of the other described categories of inorganic components).

www.iccp.org/workinggroup/inertinite-in-combustion/). The work of this group made an important contribution to establishing a unified criterion on the fused/unfused character and porous and massive/dense structure of the substance of sectioned char particles (Borrego et al., 1997), and also contributed to improving the definitions of borderline cases (such as mixed morphotypes, and solid inertoids) in the "ICCP Char Classification System" (Lester et al., 2000, 2010).

To reinforce the effectiveness of the classification, a glossary of pre-classification categories (Table 1) was defined during the 58th ICCP meeting (ICCP, 2006), and a classification of fly-ash components was established (Table 2).

2. Materials and methodology**2.1. Materials**

The materials selected for the various exercises carried out by the Fly-Ash Working Group to improve the system of classification included fly-ash from the combustion of coals of a specific coal rank (covering the entire coal rank scale), fly-ash from the combustion of complex coal blends, and also fly-ash from the combustion of coal with other materials (co-combustion).

Participants in the various exercises were asked to identify the different components of the fly-ash in photomicrographs taken with a Leica camera coupled to a Zeiss Axioplan optical microscope using the corresponding software for image analysis, in reflected white light, polarized light and with a 1λ retarder plate, using oil immersion objectives of $50\times$ magnification and $10\times$ oculars. The images of specific fly-ash components were taken at two different positions on the microscope by rotating the stage 360° to see whether the particles developed anisotropy. In addition, taking into account that the identification had to be carried out at two levels, i.e., specific particle section level and whole particle level, all the images contained a cross, an arrow or a square indicating the particular field section to be identified. This was particularly important in the case of particles with two components or very different optical characteristics.

2.2. Methodology

The methodology proposed for developing the classification of fly-ash components included a set of three round robin exercises carried out in successive years. The first exercise was developed in 2007. This exercise that had to be performed in approximately 2 h, consisted of a folder containing 210 pictures – 70% fly-ash carbons and 30% inorganics –, selected from a total of 2000 digital photomicrographs of fly-ashes derived from the combustion of pulverized feed coals and coal blends covering the entire coal rank used in European power plants, in some cases containing also petroleum and natural coke. For the analysis two pictures of each fly-ash component were included in the exercise, showing the anisotropy/isotropy of the particle. Each section of the particle to be identified and classified had been previously marked with a cross or an arrow to discriminate, for example, between particles with two components or two very different optical characteristics (Fig. 2).

The first step of the 2007 exercise was to apply the criteria based on the optical and textural properties of the components as well as their origin in order to classify the inorganic and organic components in the fly-ash by means of optical microscopy. For this purpose two main categories based on the nature of the fly-ash components were established: organic components (fly-ash carbons or unburned carbons), and mineral matter.

The criteria used to identify the fly-ash carbons were: their optical texture (whether they had an isotropic or anisotropic character); their fused, unfused or partially fused character; the structure and morphology of the fly-ash carbons (dense and massive particles *versus* porous and vesiculated, irregular *versus* spherical, e.g., crassispheeres, tenuispheres); their origin, i.e., whether carbons were derived from coal or from some other provenance such as petroleum coke. In addition, fly-ash carbons from coal could be differentiated according to the coal rank from which they were derived, and according to the precursor macerals from which they originated.

To classify the inorganic fraction and taking into account the limitations of petrographic methods in reflected light, the first step was to separate the inorganic fraction into two categories: metallic and non-metallic inorganic components. Moreover, it was suggested that the conventional criteria such as physico-optical properties (e.g., color,

Table 2
ICCP 2006–2007 fly-ash classification (established in 2006 at the 58th ICCP meeting).

	Nature	Optical texture	Character	Structure/ Morphology	Origin	
					Coal	Other
Fly-ash components	Organic fraction (Fly-ash carbons)	Unburned carbons anisotropic components	Fused carbons	Dense/massive	Low, medium and high rank coals; specific burned maceral; unburned coal; natural coke	Pet coke, tires, natural coke; <i>etc.</i>
			Unfused carbons	Porous/ vesiculate		
		Unburned carbons isotropic components	Fused carbons	Dense/massive		
			Unfused carbons	Porous/ vesiculate		
	Inorganic fraction		Metallic		Composition ^a : glassy material (alumino-silicates); quartz; oxides and hydroxides (Fe, Ca); mullite; spinels; sulfides (rare, with unburned coal); Sulfate; other inorganics.	
			Non-metallic Undifferentiate component			

^a Hower et al. (2005b).

structure and morphology, crystallinity, etc.) should be used in combination with the categories previously reported by Hower et al. (2005a). Based on the results of the 2007 exercise (discussed below), a new round robin exercise was proposed for 2009.

The second exercise in 2009 was prepared using images of fly-ash components obtained from the combustion and co-combustion of coal, biomass and coal and biomass in conditions of Pulverized Coal Combustion (PCC) and Fluidized Bed Combustion (FBC). The images were taken in the same conditions as those of the 2007 exercise. In this exercise, however, the participants had to identify and classify 279 organic and inorganic components shown in photomicrographs selected from a pool of about 1000 digital images. The participants were asked to follow the same criteria as those of the 2007 exercise (except for the partially fused qualifier that was removed) using the following sequence of classification: i) optical texture (anisotropic/isotropic); ii) fused/unfused character; iii) structure and morphology of the fly-ash carbons (massive particles, vesiculated, and with porosity, irregular, and similar features); and iv) origin. The participants in the exercise were also requested to identify and classify inorganic components (following Hower et al., 2005a) on the basis of their: i) metallic/non-metallic character; ii) physic-optical properties; iii) undifferentiated inorganic components (due to the small size of the inorganic material or the poor resolution of the microscope).

From the 2009 results, and the remarks and suggestions received, the classification of the fly-ash components was then simplified and organized into 6 levels of component identification: 3 levels relating to the identification of a specific field within a particle (e.g., Figs. 2, 4C–D, 5) and 3 levels relating to the classification of the whole fly-ash particle (Fig. 3). Thus:

- Level #1 addresses the classification of the whole particle and corresponds to the *nature of the particles*:
 - (i) Organic Components, i.e., fly-ash carbons (unburned carbons); and,
 - (ii) Inorganic Components.
- Level #2 addresses the identification of the particle field which is marked with a square instead of a cross or an arrow and is the *optical character* that may be:
 - (i) Fused: Fused character is described as a section of a particle that appears with a rounded or sub-rounded morphology, and evidences swelling and /or caking, and an absence of sharp edges due to physico-chemical changes during combustion or heating; or,
 - (ii) Unfused: Unfused character corresponds to a section of a particle

without any of the characteristics described above. The particle section is flat, has sharp edges, and can exhibit a cell-like structure (original or newly formed), or a “glove finger” type structure.

- Level #3 of this classification addresses the *optical structure* in the particle field identified. This *optical structure* can be:
 - (i) Dense (massive): A Dense/Massive structure is defined as a section of a particle without any porosity or devolatilization pores; or,
 - (ii) Porous and vesiculated: A Porous/Vesiculated structure is a section of a particle with pores resulting from thermal devolatilization (distorted pores, coalescent pores). A porous structure can be a field particle section that still retains its original porosity (cell/cavity structure).

(Note: the corresponding descriptions of “fused” or “unfused” character, dense (massive) or porous and vesiculated were also included in the classification to avoid misunderstanding)

- Level #4, *optical texture*, also addresses a specific field marked on the fly-ash component:
 - (i) Isotropic: Isotropic texture is the section of a particle that does not modify its color or color intensity when it is rotated 360°; or,
 - (ii) Anisotropic: Anisotropic texture is a section of a particle that modifies its color or color intensity when it is rotated 360°.
- Level #5 of the classification corresponds to the *origin*, with several possibilities: unburned carbons from coal, biomass, petroleum coke, among others (e.g., tires). This Level of classification addresses the whole particle.
- Level #6 refers to the *type of particle*. In this case it is necessary to consider the whole particle, applying the *ICCP Char Classification* (Lester et al., 2000, 2010).

The advantage of the proposed classification by levels is that *Levels* are independent and the petrographers can classify fly-ash components by selecting the specific level or levels of their particular interest. For the inorganic components the classification was the same as that described in the 2007 and 2009 exercises.

This new classification by levels, was checked in a new round robin exercise, carried out in 2011 at the ICCP Meeting in Porto (Portugal). In this case 25 images of fly-ash components (in two different positions) were selected. As usual, the participants had to classify each image using the first four levels (from level #1 to level #4), levels #5 and #6 being optional.

The results from each exercise (1st, 2nd and 3rd) were evaluated to check the effectiveness and accuracy of the proposed criteria for the

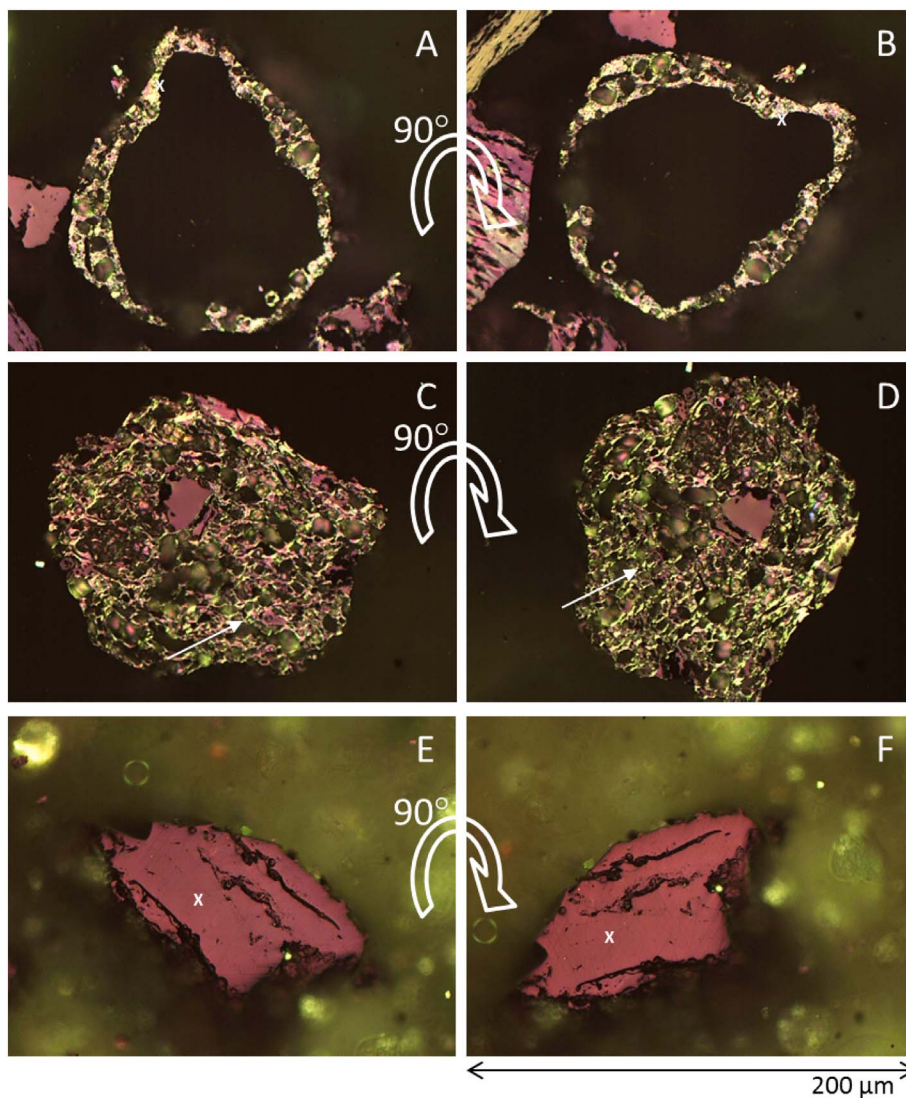


Fig. 4. Fly-ash components, 2007 exercise results. Examples of 80 to 100% level of agreement (Table 3) for the four criteria: A-B and C-D): anisotropic, fused, porous particle from coal; E-F): isotropic, unfused, dense particle from coal.

identification and classification of Fly-Ash Components by the participants in the various exercises. In the evaluation basic descriptive statistics were applied such as *mean(average)*, *median* and *mode values*, and *level of agreement* between the responses of the participants with respect to the established criteria.

3. Results and discussion

3.1. First fly-ash classification round robin exercise (year 2007)

The results from twelve participants, representing seven laboratories and seven countries (Greece, Poland, Portugal, Romania, South Africa, Spain, and the USA) showed good agreement in the classification of the organic components (> 80%). That is, most of the images of organic components that had to be analyzed showed a level of agreement among the participants of above 80% using the average, median and mode values, Table 3). However, poor agreement was obtained in the classification of inorganic components. The average, median and mode values were below 75% (Table 3) which meant that the analysts' performances in identifying and classifying the inorganic fraction were not satisfactory in this round robin.

In relation to optical texture (with two qualifiers: isotropic/anisotropic) the participants had found that 56% of the fly ash carbons were anisotropic and 44% were isotropic (see amount of particles assigned to each qualifier in Table 3). The participants showed a high level of

agreement between 80 and 100% (> 80%, see agreement classes in Table 3) in the assignments for 65% of the carbons with respect to these criteria.

As for structure (dense/porous) and origin (coal/other) the participants also showed a high level of agreement (above 80%, see average, median and mode values in Table 3 for analysts' performance), while optical character (fused/unfused) resulted in a low level of agreement (< 80%; Table 3), (examples in Fig.5). For optical character the participants in the round robin decided that 40% of the particles were fused carbons; 31% were unfused carbons and 29% were classified as partially fused carbons (see amount of particles assigned to each qualifier in Table 3). The level of agreement between the participants in the responses for this criterion is low. 35% of the carbons were classified with a level of agreement between 80 and 100%; 29% with a level of agreement between 65 and 80%; 31% of the images with a level between 50 and 65% and finally 5% of the images with a level of agreement lower than 50% (see agreement classes in Table 3). The "partially unfused" qualifier was responsible for the worst results (see analysts' performance in Table 3) of the optical character criterion.

As mentioned above, most of the inorganic components were classified with a low level of certainty, since only 30% of the pictures (see agreement classes in Table 3) showed a level of agreement above 80%, 73% being the average, median and mode values (see analysts' performance in Table 3). This was because the inorganic components could be classified according to three qualifiers (metallic, non-metallic and

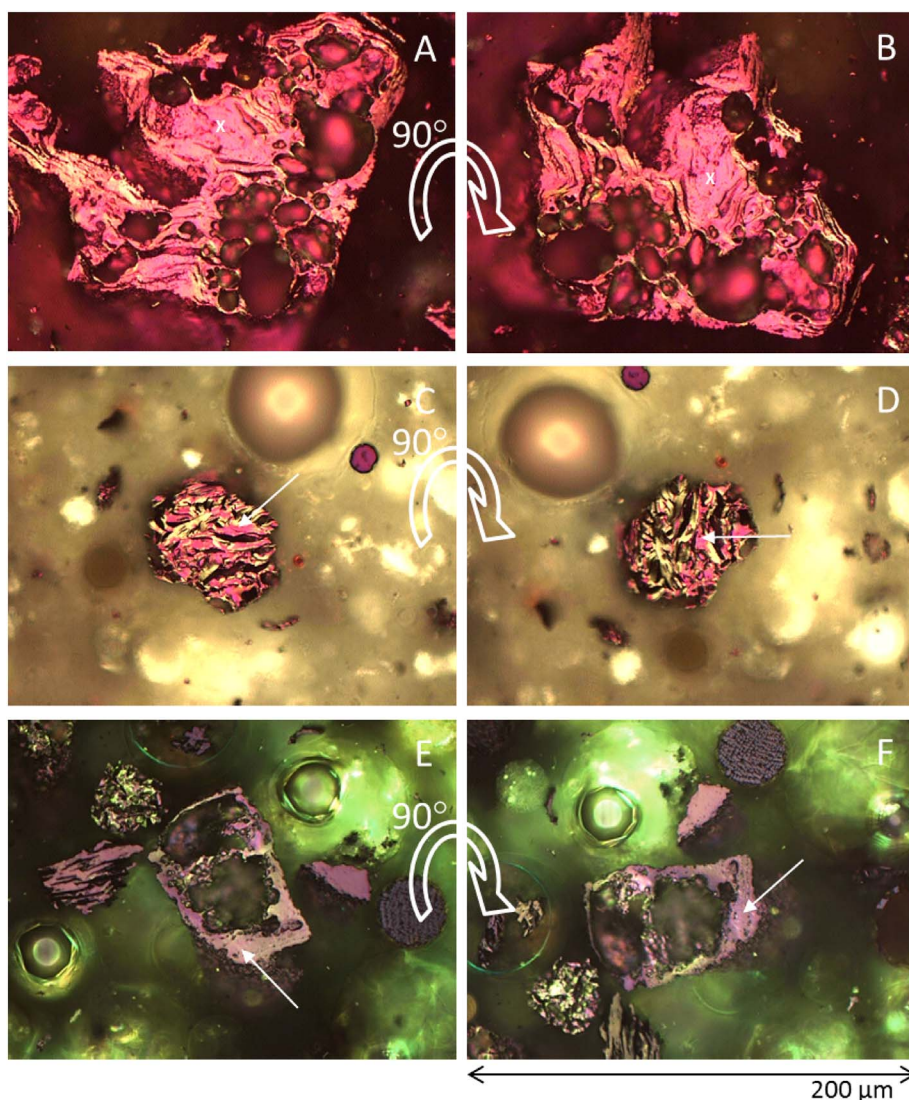


Fig. 5. Fly-ash components, 2007 exercise results. Examples of < 50% level of agreement for the four criteria (Table 3): A-B): anisotropic “??”, unfused “??”, dense particle from coal; C-D): anisotropic, fused “??”, porous “??” particle from coal “??”; E-F): anisotropic “??”, fused “??”, porous particle from coal.

undifferentiated) and because of the lack of experience of some analysts who were not able to assign the inorganics to the category of metallic or non-metallic, and classified the ambiguous inorganic particles in the category of undifferentiated inorganics (examples in Fig. 6).

The general conclusion drawn from the 2007 exercise was that the proposed criteria for identifying and classifying the fly-ash components were: correct, effective and easily applicable (TSOP Newsletter #25/3, 2008. <http://www.tsop.org> and Minutes of Commission III, ICCP Meeting, Victoria 2007). However, it was considered that the “partially fused” qualifier should be removed in the next round robin exercise when using fly-ashes from combustion and co-combustion. The same proposal was made for the third qualifier (undifferentiated inorganics) used for the identification of inorganic components.

3.2. Second fly-ash classification round robin exercise (year 2009)

The main objective of this exercise was to check the criteria established for classifying the fly-ash components in fly-ashes derived from combustion of coals, co-combustion, and combustion of biomass in European and US power plants in conditions of pulverized coal combustion (PCC), fluidized bed combustion (FBC), stoker boilers, and heating boilers. Some feed fuels also contained petroleum coke. For this exercise the criteria were simplified as follows:

- Classification of fly-ash components based on their nature: 1) *Organic Components*: fly-ash carbons (unburned carbons); and 2) *Inorganic Components*.
- Classification of fly-ash carbons according to: i) Their *optical texture*: isotropic/anisotropic texture; ii) *Character*: fused/unfused/partially fused; iii) *Structure*: dense/massive vs. porous/vesiculated; iv) *Origin*: coal/biomass/other.
- Classification of *Inorganic components* according to: i) Their *character*: metallic/non-metallic; ii) *undifferentiated*.

Although in this proposal the qualifiers “partially fused” for unburned carbons and “undifferentiated” for inorganics were still kept, it was recommended that they should not be used and that the sections and particles observed should be assigned to the “fused” or “unfused” and to the “metallic” or “non-metallic” qualifiers.

This exercise was performed on 279 images (165 of unburned carbons and 114 of inorganics) and the identification and classification had to be performed following the pre-established criteria on the section of the particle marked with a cross or an arrow (examples in Figs. 2, 4, 7). This was particularly important in the case of particles with two components or very different optical characteristics. A statistical evaluation of the results revealed an improvement in the identification of inorganic components with respect to those obtained in the exercise of 2007. On the other hand, there was a good agreement in the

Table 3

Results of the first ICCP round robin exercise (year 2007) on fly-ash classification.

Analysts' performance															
Analyst number	A1	A2	A3	A4	A5	A7	A10	A11	A12	A14	A15	A17	Average	Median	Mode
Optical texture (%)	89	80	86	90	83	72	77	77	75	83	85	90	82	83	90
Character (%)	81	79	79	87	71	66	79	73	63	69	81	71	75	76	79
Structure (%)	86	86	85	89	85	84	92	89	77	84	78	79	85	85	86
Origin (%)	97	94	91	91	92	90	94	62	97	93	86	93	90	93	97
Total organic fraction (%)	88	85	85	89	83	78	86	75	78	82	83	83	83	83	83
Total inorganic fraction (%)	73	70	73	95	80	70	62	78	47	65	78	82	73	73	73
Analyst total (%)	85	82	83	90	82	76	81	76	72	79	82	83	81	82	82

Amount of particles assigned to each qualifier															
	Anisotropic	Isotropic	Fused	Unfused	Partially Fused	Massive	Porous	Coal	Others	Metallic	Non-Metallic	Undifferentiated			
Optical texture (%)	56	44													
Character (%)			40	31	29										
Structure (%)						47	53								
Origin (%)								88	12						
Inorganic Fraction (%)										38	48	14			

Agreement classes									
Optical texture	Character	Structure	Origin	Inorganic Fraction					
%	%	%	%	%	%	%	%	%	%
≥ 50 < 65	10	< 50	5	≥ 50 < 65	13	≥ 50 < 65	1	< 50	3
≥ 65 < 80	25	≥ 50 < 65	31	≥ 65 < 80	15	≥ 65 < 80	8	≥ 50 < 65	27
≥ 80 ≤ 100	65	≥ 65 < 80	29	≥ 80 ≤ 100	72	≥ 80 ≤ 100	91	≥ 65 < 80	40
		≥ 80	35					≥ 80	30

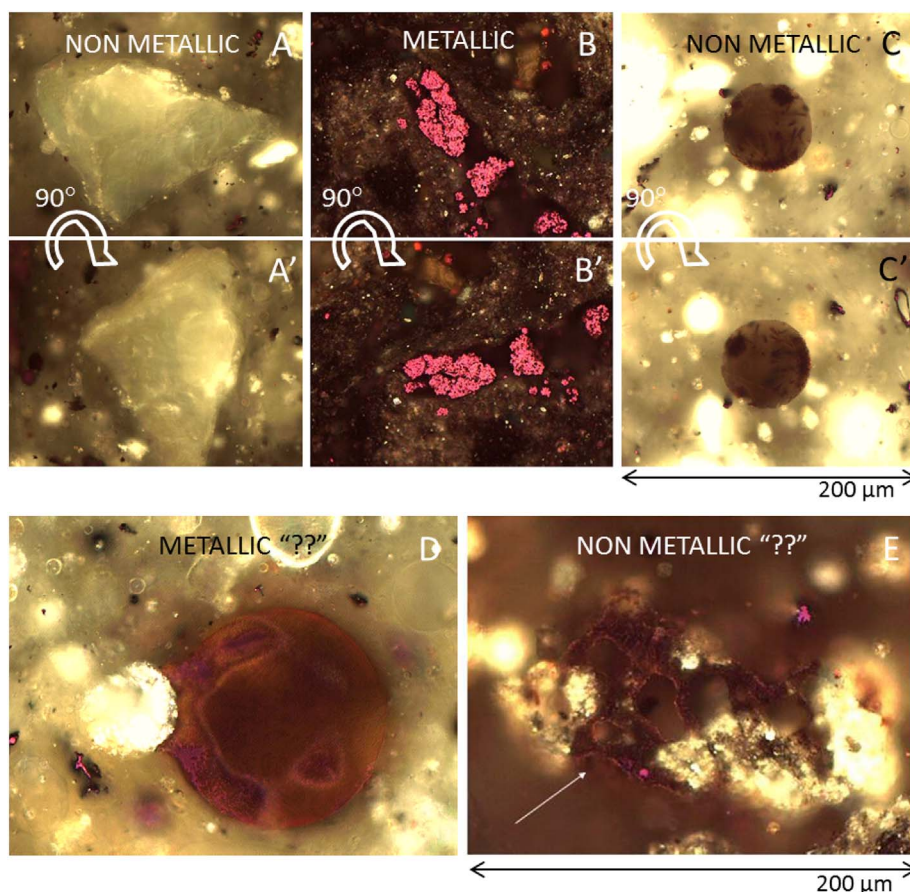


Fig. 6. Inorganic components in fly-ash, 2007 exercise results. Examples of % level of agreement for the metallic or non-metallic category (see agreement classes in Table 3): A, B and C): 80–100%; D and E): examples of < 50%.

identification and classification of the organic components with average, median and mode values of 81%, 80% and 78%, respectively (see analysts' performance in Table 4); and for inorganic components in all cases > 80% (Table 4) indicating that most participants managed to

assign the mineral matter to the metallic or non-metallic categories successfully.

In the case of the fly-ash carbons, in this exercise high agreement (≥ 80%) was achieved in optical texture (isotropic/anisotropic), character

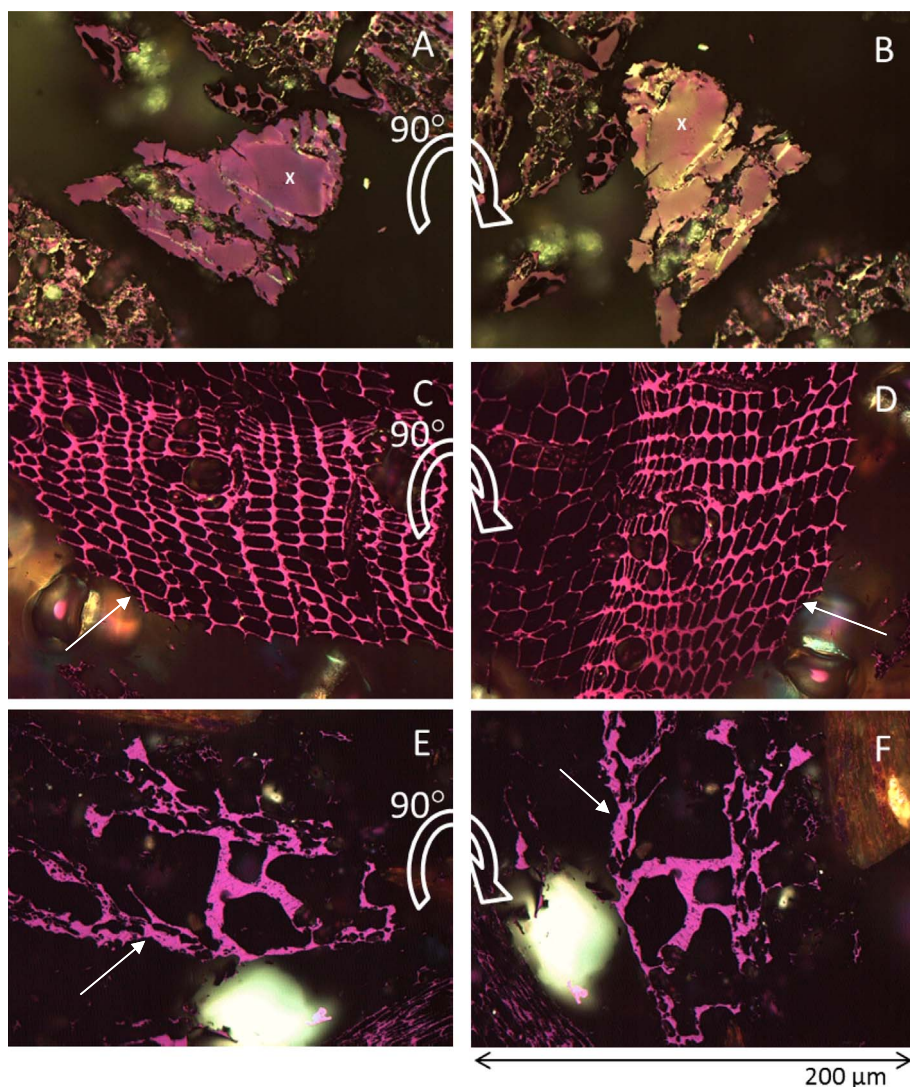


Fig. 7. Organic components in fly-ash, 2009 exercise results. Examples of 80–100% level of agreement (Table 4) in the marked field: A-B): anisotropic, unfused, and dense particle section from coal; C-D): isotropic, unfused, and porous particle from biomass; E-F): isotropic, fused, and porous particle from biomass.

(fused/unfused) and origin (coal/other) (see average, median and mode values for these qualifiers in analysts' performance of Table 4 and Fig. 7). As in the previous case the participants classified most of the fly-ash carbons as fused or unfused, avoiding the qualifier “partially fused” (see amount of particles assigned to each qualifier in Table 4). However, the worst level of agreement (< 75%) was achieved for the “structure” criterion (average, median and mode values for structure in analysts' performance of Table 4). This was due to the type of marker used. When an arrow or a cross is used as a marker of a specific field particle that is to be classified, those markers actually indicated only a point and participants were required to look at the whole particle. This led to bias in the assessment of the results and lowered the corresponding level of agreement on the porous/massive qualifiers (Table 4). In addition the degree of difficulty in identifying the particles largely increased with respect to the 2007 exercise. However, despite this, the 2009 results confirmed again that the criteria proposed for identifying and classifying the fly-ash components were correct, effective and easily applicable to the different combustion fly-ashes.

Despite the acceptable results, in the discussions of the Gramado 2009 ICCP Meeting, the removal of “cenosphere, network”, and similar terms belonging to the ICCP Char Classification System (Lester et al., 2000, 2010) for the classification of fly-ash was suggested. In addition a request was also made for the modification of the pre-classification and the setting up of several different, and independent levels: level #1 for the nature of the fly-ash components; level #2 for the optical texture,

character and structure/morphology; level #3 for the type of particle (at this point ICCP char classification can be applied); level #4 for the origin of the fly-ash carbons; level #5 for the rank of the coal-derived carbon; and, level #6 for “other”. During the Belgrade ICCP Meeting (2010) a set of new modifications was requested for the fly-ash classification including: i)- to improve the level of the description by indicating that some of these levels are only concerned with particle surface identification (as in the case of maceral analysis), ii)- to keep one level for classifying the total particle (as in the ICCP Char Classification) by describing the characteristics to be analyzed including graphical examples, and iii)- to replace the cross/arrow by an empty square on the specific particle surface to be classified. In addition it was also decided not to use the qualifiers “partially fused” and “undifferentiated” for the character of unburned carbons and the inorganics respectively.

3.3. Third fly-ash classification round robin exercise (year 2011)

A new round robin exercise was proposed for the years 2011–2012. In this exercise for which 25 pictures of fly-ash components were used the independent criteria to be successively applied were structured on 6 levels as follows (Table 5; <http://www.iccop.org/documents/atlas-of-fly-ash-occurrences.pdf>): with 3 levels addressing the identification of the small local particle field marked with a square (Fig. 8) for particle surface identification, and 3 levels directed at the whole particle in the

Table 4

Results of the second ICCP round robin exercise (year 2009) on fly-ash classification.

Analysts' performance															
Analyst number	A1	A2	A3	A4	A5	A7	A10	A12	A14	A15	A17	A18	Average	Median	Mode
Optical Texture (%)	82	81	84	91	93	85	85	87	94	75	92	94	87	86	85
Character (%)	90	79	70	87	76	72	81	90	72	88	78	92	81	80	90
Structure (%)	70	62	73	73	55	78	68	48	70	74	73	76	68	72	73
Origin (%)	95	82	79	78	92	76	93	86	84	85	95	95	87	86	95
Total Organic Fraction (%)	84	76	77	82	79	78	82	78	80	81	85	89	81	80	78
Total Inorganic Fraction (%)	92	97	95	89	87	84	89	54	76	82	80	87	84	87	89
Analyst Total (%)	86	80	80	83	80	79	83	73	79	81	83	89	81	81	80

Amount of particles assigned to each qualifier															
	Anisotropic	Isotropic	Fused	Unfused	Partially Fused	Massive	Porous	Coal	Biomass	Others	Metallic	Non-metallic	Undifferentiated		
Optical Texture (%)	49	51													
Character (%)			56	44	0										
Structure (%)						55	45								
Origin (%)								72	26	2					
Inorganic Fraction (%)											35	64	1		

Agreement classes															
Optical Texture	Character		Structure		Origin		Inorganic Fraction								
%	%	%	%	%	%	%	%	%							
≥ 50 < 65	5	< 50	1	≥ 50 < 65	19	< 50	2	< 50	2						
≥ 65 < 80	18	≥ 50 < 65	17	≥ 65 < 80	24	≥ 50 < 65	8	≥ 50 < 65	14						
≥ 80 ≤ 100	77	≥ 65 < 80	28	≥ 80 ≤ 100	57	≥ 65 < 80	17	≥ 65 < 80	21						
		≥ 80	54			≥ 80	73	≥ 80	63						

image (see definitions in Table 1).

Level #1 is directed at the whole particle and is based on the *Nature* of the particles: i) *organic components*: fly-ash carbons (unburned carbons); or, ii) *inorganic components*.

Level #2 is directed at particle field identification, and refers to the *Optical character* of the field section which may be: i) *fused*; or, ii) *unfused*.

Level #3 is directed at particle field identification and corresponds to the *Optical structure* which may be: i) *dense/massive*; or, ii) *porous/vesiculated*.

Level #4 is directed at particle field identification and corresponds to the *Optical texture* which may be: i) *isotropic*; or, ii) *anisotropic*.

Level #5 is directed at the whole particle and refers to the *Origin* of the particle that may be: i) *coal*; ii) *biomass*; iii) *petroleum coke*; and; iv) *others* (such as tires, etc.)

Level #6 is directed at the whole particle and corresponds to the *Type of particle*. To describe the Type of particle it is necessary to apply the ICCP Char Classification System (<http://www.iccop.org/workinggroup/inertinite-in-combustion/>) published under Lester et al.

(2000, 2010).

In 2011 during the Porto ICCP Meeting all the participants at the meeting, most of them inexperienced in fly-ash microscopy were asked to perform an exercise on the classification of fly-ash components during a session lasting 25 min (one minute per exercise slide) and in 2012, the participants in the working group were also requested to perform the same exercise. The assessment of the results obtained from the 2011 round robin exercise including all the suggested modifications to the pre-existing classifications showed that the total analysts' performance of the WG Non-members was lower than that of the WG members, i.e., they obtained lower mean, median and mode values, which is explained by the lack of experience of most of the non-members of this ICCP working group with this type of round robin and with this topic. Consequently the final assessment of the results was only carried out using the results provided by the Fly-Ash Classification Working Group members. In this case there was excellent agreement (96%, 96%, 100% for the average, median and mode values, respectively) for the identification and classification of fly-ash components with regard to the *nature* criterion (analysts' performance in Table 6,

Table 5

Fly-Ash Working Group. Classification of Fly-Ash Components: proposed for the 2011 exercise.

	Level #1	Level #2	Level #3	Level #4	Level #5	Level #6
	<i>Nature</i>	<i>Character</i>	<i>Structure / Morphology</i>	<i>Optical texture</i>	<i>Origin</i>	<i>Type of particle</i>
Fly-ash components	Organic fraction (fly-ash carbons)	Fused	Dense / Massive	Isotropic	Coal Biomass Pet coke Other	Apply the ICCP Char Classification*
				Anisotropic		
			Porous / Vesiculate	Isotropic		
				Anisotropic		
		Unfused	Dense / Massive	Isotropic		
				Anisotropic		
			Porous / Vesiculate	Isotropic		
				Anisotropic		
	Inorganic fraction					

*Lester et al. (2000, 2010)

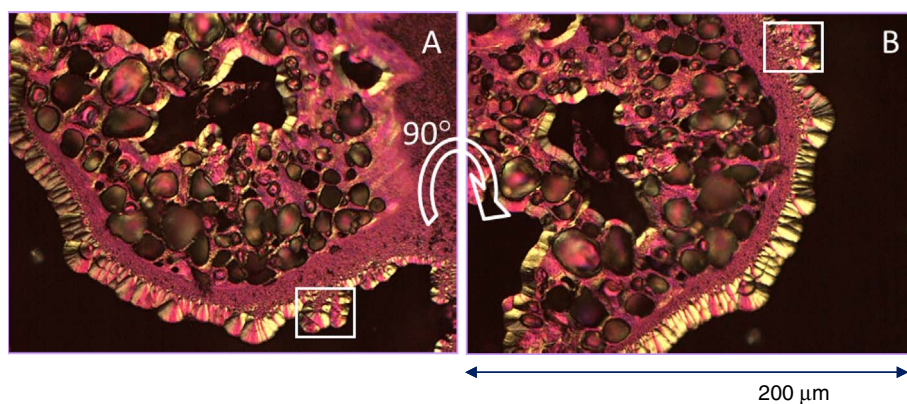


Fig. 8. Fly-ash components, 2011 exercise results. Example of high level of agreement (> 80%) for the five levels considered: A-B): organic, fused, dense, and anisotropic particle from coal (the rim is pyrolytic carbon).

Level # 1: whole particle: Organic
 Level # 2: particle surface identification: Fused
 Level # 3: particle surface identification: Dense
 Level # 4: particle surface identification: Anisotropic
 Level # 5: whole particle: Coal

and Fig. 8). The criteria for the classification of the fly-ash carbons namely *character*, *structure*, *optical texture* and *origin* showed levels of agreement of 62%, 70%, 78%, 56% for the average value; 64%, 72%, 80%, 56% for the median value and, 60%, 72%, 80% and 60% for the mode value, respectively, with the best corresponding to optical texture (*isotropic/anisotropic* fly-ash carbon) and the poorest to *origin* (Table 6). The positive trend found in the level of agreement for the various criteria used in the identification and classification of the fly-ash components may be due to the small number of images used in this exercise.

Additionally, it was concluded that an increase in the number of exercises to be performed would not increase the level of agreement. Level #6 (*Type of particle* in the ICCP Char Classification) was not included in the results assessment because it was not mandatory.

3.4. Precision and bias of the analysts: suitability of the proposed criteria for fly-ash component classification

To obtain a better idea of the performance of the analysts in the

Table 6

Results of the third ICCP round robin exercise (year 2011) on fly-ash classification.

Analysts' performance														Average	Median	Mode
Analyst number	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13			
Nature (%)	100	96	100	92	100	88	96	92	100	96	92	96	100	96	96All the numbers should be centered in the rows	100
Character (%)	72	68	60	28	68	60	80	64	68	64	80	44	72	62	64	60
Structure (%)	72	68	68	56	72	80	52	84	76	92	76	52	72	70	72	72
Texture (%)	80	80	92	68	80	68	72	84	80	80	80	80	72	78	80	80
Origin (%)	64	64	64	60	48	52	56	60	52	68	60	48	60	56	56	60
Analyst Total (%)	78	75	77	61	74	70	71	77	75	80	78	64	75	72	75	75

Amount of particles assigned to each qualifier											
Nature (%)	Inorganic	Organic	Fused	Unfused	Dense	Porous	Isotropic	Anisotropic	Coal	Biomass	Others
20	80										
Character (%)			50	50							
Structure (%)					42	58					
Texture (%)							38	62			
Origin (%)									48	36	16

Agreement classes									
Nature	%	Character	%	Structure	%	Texture	%	Origin	%
≥ 50 < 65	4	< 50	0	≥ 50 < 65	20	≥ 50 < 65	20	< 50	4
≥ 65 < 80	0	≥ 50 < 65	24	≥ 65 < 80	36	≥ 65 < 80	12	≥ 50 < 65	28
≥ 80 ≤ 100	96	≥ 65 < 80	40	≥ 80 ≤ 100	44	≥ 80 ≤ 100	68	≥ 65 < 80	36
		≥ 80	36					≥ 80	32

Table 7
Group mean and standard deviation of the various classification criteria.

		Group mean	Standard deviation
Nature	Inorganic	4.54	1.127
	Organic	20.46	1.127
Character	Fused	12.31	5.186
	Unfused	9.15	3.955
Structure	Dense	11.85	3.976
	Porous	11.00	3.416
Optical texture	Isotropic	10.54	2.602
	Anisotropic	12.31	2.175
Origin	Coal	12.38	3.709
	Biomass	4.15	1.281
	Other	4.85	3.184

identification and classification of the fly-ash components using the proposed criteria it was decided to apply ICCP statistics (<http://www.iccop.org/accreditation/statistical-evaluation-in-detail/>). These statistics are usually applied to the Accreditation Programs of the ICCP and they are based on the mean of the group of analysts and on the standard deviation against the group means (multiple standard deviations). This enabled an assessment of the accuracy and bias of the analysts in the identification and classification of the fly-ash components.

The parameters used for this evaluation (whose definitions and meanings are in the website mentioned above) were the Group Mean (GM), the Group Standard Deviation (GSD), the Signed Multiple of the Standard Deviation (SMSD) calculated against the GM and the GSD, and the Averaged Signed Multiples of the Standard Deviation (ASMSD). This latter parameter is a measure of the bias of the group means and indicates the degree of consistency of an analyst. Other parameters included in this evaluation were the Unsigned Multiple of the Standard Deviation (UMSD) which is the absolute value of SMSD, and the corresponding Average Unsigned Multiple of the Standard Deviation (AUMSD). This parameter is an indicator of the dispersion of the group means and a measure of the accuracy of the analyst. If the dispersion with respect to the mean values (AUMSD) is below 1.5 (value used as a cut-off in the ICCP Accreditation Programs), the results are acceptable.

According to this, the GM, GSD, the SMSD (and UMSD) were calculated taking into account each qualifier of the various established criteria and also the AUMSD and ASMSD for each participant as can be seen in Tables 7 and 8. The results in Table 8 show that all the analysts had an AUMSD value < 1.5 and in all cases the ASMSD indicate a minor bias ($\pm < 0.5$).

Table 8
Accuracy and bias of results calculated against the group mean and standard deviation for the various classification criteria.

Analysts	Nature		Character		Structure		Optical texture		Origin			AUMSD ^b	ASMSD ^c	Bias
	Inorganic	Organic	Fused	Unfused	Dense	Porous	Isotropic	Anisotropic	Coal	Biomass	Other			
	SMSD ^a	SMSD ^a	SMSD ^a	SMSD ^a	SMSD ^a	SMSD ^a	SMSD ^a	SMSD ^a	SMSD ^a	SMSD ^a	SMSD ^a			
#1	0.410	−0.410	0.326	−0.797	−0.213	−0.586	−0.976	−0.141	0.166	0.661	−0.894	0.507	−0.223	Low
#2	−0.478	0.478	−0.638	0.973	1.045	−1.171	0.946	−0.601	0.975	−0.120	0.048	0.679	0.132	Low
#3	0.410	−0.410	1.869	−1.556	1.799	−1.464	−0.591	1.698	0.436	−0.901	−0.580	1.065	0.065	Low
#4	−0.478	0.478	−1.023	−0.545	0.542	0.878	−0.591	−0.141	−0.104	−0.120	0.048	0.450	−0.096	Low
#5	0.410	−0.410	0.133	−0.545	0.290	−1.171	−0.976	−0.141	−1.721	−0.120	1.618	0.685	−0.239	Low
#6	−2.253	2.253	−0.831	1.225	0.039	0.586	1.715	−1.981	−0.643	−0.120	−0.580	1.111	−0.054	Low
#7	−0.478	0.478	0.133	−0.292	−2.225	2.049	−1.744	1.238	0.975	−1.681	−0.894	1.108	−0.222	Low
#8	−1.366	1.366	−0.831	1.225	−0.213	0.293	0.177	−0.141	0.166	1.441	−0.894	0.737	0.111	Low
#9	0.410	−0.410	1.098	−1.050	−0.213	0.293	−0.207	0.318	0.436	−0.120	0.362	0.447	0.083	Low
#10	1.297	−1.297	0.519	0.214	−0.213	0.878	1.330	−0.601	0.436	1.441	−1.208	0.858	0.254	Low
#11	0.410	−0.410	0.905	−0.292	0.793	−0.293	0.562	0.318	1.514	−1.681	0.048	0.657	0.170	Low
#12	1.297	−1.297	−1.795	1.731	−1.219	0.293	−0.207	1.238	−1.721	0.661	0.990	1.132	−0.003	Low
#13	0.410	−0.410	0.133	−0.292	−0.213	−0.586	0.562	−1.061	−0.913	0.661	1.932	0.652	0.020	Low

^a Signed multiple of the standard deviation (SMSD).

^b Mean of the sum of the unsigned multiples of the standard deviation (AUMSD), it is a measure of accuracy.

^c Mean of the signed multiple of the standard deviation (ASMSD), it is an indicator of bias.

The values of AUMSD for all the analysts and the classification criteria indicate that the data offer a consistent basis for assessing the quality of the selected criteria and the procedure followed for classifying the components of fly-ash.

Taking into account the results obtained a final classification was established as reported in <http://www.iccop.org/documents/atlas-of-fly-ash-occurrences.pdf> and shown in Table 5. This scheme is easy to handle and permits a rapid identification and classification of the components of fly-ash produced by the combustion of coals and other fuels.

3.5. Level #1 of the petrographic classification of fly-ash components: disambiguation

The “Petrographic Classification of Fly Ash Components” described here and developed by the corresponding Working Group in Commission III of the ICCP (Suárez-Ruiz et al., 2015) is meant to be universal. However, coal is a heterogeneous material and coal fly-ash reflects this heterogeneity. Due to this heterogeneity, as well as the combustion process and conditions, the fly-ash organics and inorganics and their associations may be grouped in general and in more or less specific terms, but there are ambiguous situations.

Level #1 of the “Petrographic Classification of Fly Ash Components” is described as being mainly directed at whole particle identification and corresponds to the nature of the particles: i) Organic Components (unburned carbons); and ii) Inorganic Components. This means that a particle at level #1 is classified as a whole. However, it may be a particle that is totally (100%) composed of carbonaceous matter or totally (100%) composed of inorganic matter (Fig. 9A, B). In such cases it is very easy to decide and classify the particle from the point of view of its “nature”. Nevertheless, there are mixed organic-inorganic particles with a variable volume % of either component (organic and inorganic, Fig. 9C–F). The assignment of “nature” to this kind of particles may be more problematic if the whole particle is being considered. In this case and in a quantitative analysis involving the use of a point counter the “nature” assignment should be carried out with respect to the point that is marked by the cross-hair. If the cross-hair is pointing at carbonaceous material, then the nature will be organic, if the cross-hair is pointing at mineral matter, then the nature will be inorganic.

4. Conclusions

A new system for the petrographic classification of fly-ash

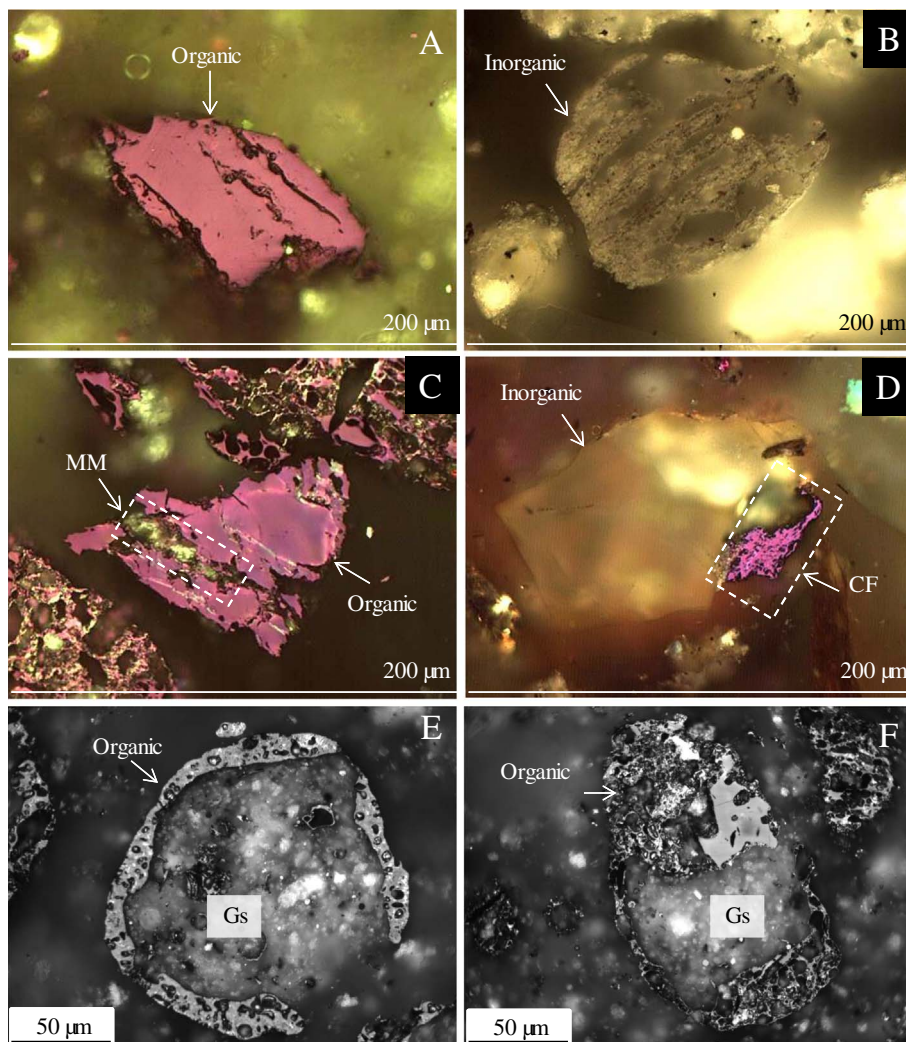


Fig. 9. Level #1, “nature”: A) Organic: 100% carbonaceous matter; B) Inorganic: 100% mineral matter (partially baked clay); C) Organic: carbonaceous particle (inertoid) with less than < 50% mineral matter (MM); D) Inorganic: particle > 50% mineral matter (quartz) with a char/carbonaceous fragment (CF) attached; E) Organic: char cenosphere filled with glassy spheres as inorganics (Gs); F) Organic: char filled with glassy spheres inorganics (Gs).

components has been developed by the Fly-Ash Working Group, Commission III of the ICCP. This classification system is based on a small number of easily applicable microscopic criteria that were established after three round robins exercises successively performed by petrographers involved in this task.

The fly-ashes used in the various round robins were obtained from the combustion of single coals of varied rank, coal blends, and coals blended with other fuels (biomass, petroleum coke) using different operating technologies and conditions (pulverized coal combustion, fluidized bed combustion, stoker boilers, and heating boilers). Images taken of the fly-ash components were used in a series of round robin exercises.

After the evaluation of results from the first two exercises (performed in 2007 and 2009) using descriptive statistics, three main issues were raised. The first one was to decide on how to apply the pre-selected criteria: on the whole particle or on a section of the particle. This work has demonstrated that when particles are being classified by microscopic examination it is necessary to establish first whether the classification should take into account the whole particle or the classification should be based on the field section on which the cross-hair is falling. This distinction is important because most of the particles to be classified, particularly organic particles, like fly-ash are heterogeneous, and displaying several optical properties in the same particle.

The second and third issues were to reduce the number of qualifiers included to a specific criterion to improve the accuracy and performance of the analysts and ensure a similar quality of results. Therefore,

the “partially fused” and “undifferentiated inorganics” qualifiers were removed from the criteria “character of unburned carbons” and “inorganics”, respectively.

The initial criteria proposed for classifying the fly-ash carbons in the first two round robins were then modified leaving only the appropriate criteria that best describe the optical characteristics of an unburned carbon. These criteria, for fly-ash carbons, are independent of each other and were subdivided into 6 levels of identification, three directed at the whole particle (nature, origin and type of fly-ash component) and three directed at a specific particle field (character, structure and optical texture of the fly-ash carbons). Each criterion contains two qualifiers with the exception of “origin” which has three qualifiers taking into account the different feed fuels. For inorganics, considering the limitations of optical microscopy, the classification criteria are based on their composition with two qualifiers: metallic and non-metallic.

The criteria for classifying the fly-ash components were tested, in 2011, in a third round robin exercise and after the application of two evaluation procedures, the second one based on the statistical parameters used in the existing ICCP accreditation programs (www.iccop.org), yielded the most satisfactory results for classifying the components with a good accuracy and only a minor bias. Therefore, the proposed criteria were found to be valuable for identifying, classifying and describing the optical properties of the components of fly-ash.

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